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AFTB

AUTOMATION OF A DUAL OPEN COLUMN CHROMATOGRAPHIC CLEANUP TECHNIQUE FOR SAMPLES CONTAINING CHLORINATED DIBENZO-p-DIOXINS AND DIBENZOFURANS

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A technique to automate the cleanup stage of samples analyzed for ultra trace levels (ppq) of chlorinated dibenzp-p-dioxins (PCDDs) and dibenzofurans(PCDFs) has been researched by the Ontario Ministry of the Environment (MOE). The Fluid Management System (FMS - Nortech Controls) replaces a manual two stage open column cleanup technique used in the Dioxin Unit.

The FMS used in the Dioxin Unit at the MOE processes five samples unattended and automatically through a set of two columns. The first contains three treated silica gel packings and the second column contains alumina. Two fractions per sample are collected, the first contains polychlorinated biphenyls (PCBs) while the second fraction contains PCDDs and PCDFs.

This automated system saves the chromatographer a full day in the sample preparation process. When done manually, the dual column cleanup takes two day; one day per column set with a solvent concentration step in-between columns. The FMS will process one sample extract through two columns in one hour. Samples are run in series, so a set of five samples takes five hours. Once all columns are packed and sample extracts and glassware are in place the system is ready to perform the cleanup unattended.

This system has been optimized for dioxin and furan recoveries. These recoveries are equal to or greater than those achieved by manual column chromatography. No carryover has been observed provided column capacity has not been exceeded.

Method

Hand packed silica and alumina columns were placed in the positions shown in Figure 1. The first step in this automated cleanup was to wet the columns with hexane before sample addition. When this task was complete the sample wass taken from a roundbottom flask and placed on the column. After sample addition, clean hexane was pumped from the sovent reservoir into the roundbottom before being eluted through the column. This step rinsed the roundbottom to help maximize surrogate recoveries.

Once all hexane rinses passed through the columns (silica and alumina) the dioxins and furans were present only on the alumina. Any PCB interferences present were removed with the 2% dichloromethane(DCM):hexane (v/v) elution of the alumina column. The PCDDs and PCDFs were then collected by elution with 25%

DCM:hexane (v/v). After collection was complete all of the common lines were flushed with hexane.

All of the steps described were carried out using the FMS which has a microprocessor to control the valve switching as well as the pumping system. Once a progam had been written for each sample the valving control comands were saved and recalled at a later date.

Method development was carried out by spiking clean solvent with a $^{13}C_{12}$-PCDD surogate standard that had a 2,3,7,8 substituted isomer in each of the congener groups from tetra through to octa. The spiked solvent was then run through the columns as described above and the collected fractions were analyzed for recovery of the surrogate standard. Initial analyses were carried out by GC-ECD (Hewlett Packard 5890). Some of the carryover check samples were run by GC-MS (Finn 4500).

Experimental

An optimized mannual method was used as a baseline for setup of the automated method. Recoveries of the PCDDs using the automated method were optimized using the silica columns alone (Table 1) followed by the complete silica/alumina system (Table 2)

Results and Discussion

TABLE 1 Percent Recovery of Spiking Solution on Silica Columns using FMS

Isomer	Volume of Hexane (mL)	
	130	160
$^{13}C_{12}$T4CDD	64	88
$^{13}C_{12}$P5CDD	56	73
$^{13}C_{12}$H6CDD	65	82
$^{13}C_{12}$H7CDD	67	101
$^{13}C_{12}$OCDD	63	75

TABLE 2 Percent Recovery of Spiking Solution on Dual Columns using FMS

Isomer	Volume of 2%DCM:hexane/ 25% DCM:hexane		
	20/50	20/50[1]	20/50[2]
$^{13}C_{12}$T4CDD	87	103	49
$^{13}C_{12}$P5CDD	66	95	56
$^{13}C_{12}$H6CDD	70	107	44
$^{13}C_{12}$H7CDD	102	124	50
$^{13}C_{12}$OCDD	79	103	48

1 A five minute delay before elution of the alumina column was programed into the method to ensure all of the hexane eluted off the column before addition of the 2%DCM:hexane.

2 This column set was spiked with a flyash extract as well as the surrogate spike. The levels of dioxins and furans in the flyash were approximately 5 to 50 ng of tetra through octa.

Overall the recoveries are acceptable but should be improved to handle high level samples more efficently. The high levels of dioxins and furans in the sample may have overloaded the columns.

A carryover study was done at the same time. The fraction collected from the column set following the flyash extract contained approximately 0.1 ng of hexa through octa dioxin. This works out to be a 0.2% carryover. If the volume of hexane used to rinse to common lines is increased the carryover may be eliminated.

Fine tuning of the method is still needed. Priliminary results look promising. The advantages to this system are significantly reduced preparation times as well as the reduced human exposure to highly toxic chemicals.

FIGURE 1 AUTOMATED CHROMATOGRAPHIC TECHNIQUE FOR ISOLATION OF CHLORINATED DIBENZO-p-DIOXINS AND DIBENZOFURANS